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Comments on the SURFplus reactive burn model

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1 Introduction

The SURFplus reactive burn model [Menikoff and Shaw, 2012] is intended for heterogeneous solid HE that produce an excess amount of carbon. It utilizes a fast hotspot reaction (SURF model, see [Menikoff and Shaw, 2010] and [Menikoff, 2017, App A]) plus a second slow reaction for the energy release from carbon clustering. The fast reaction dominates shock initiation, though the fast rate parameters are slightly affected by the late energy release from the slow reaction. The slow reaction has a significant affect on propagating detonation waves.

Propagating detonation waves are characterized by the curvature effect; *i.e.*, detonation speed D_n as function of the local front curvature κ, see [Bdzil and Stewart, 2007] and references therein. Figure 1 compares the normalized curvature effect for 2 explosives, one without and the other with a second slow reaction, the HMX based PBX 9501 and TATB based PBX 9502, respectively. The $D_n(\kappa)$ curves have a qualitative different shape. This results from the sensitivity of the
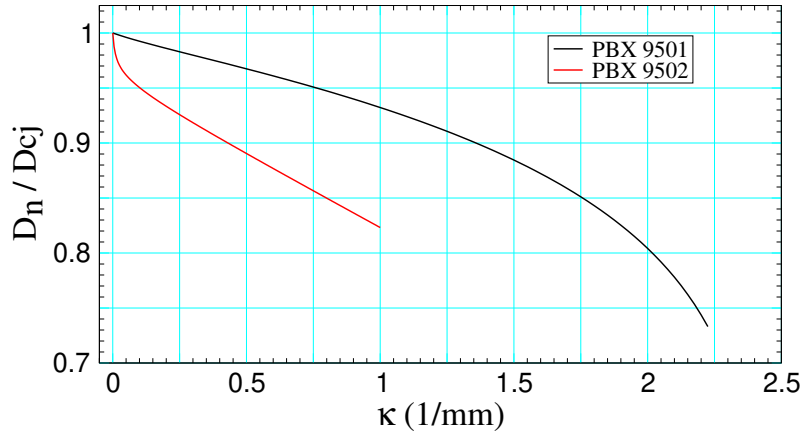

Figure 1: Examples of the normalized curvature effect for explosives without and with a second slow reaction, PBX 9501 and PBX 9502, respectively; [see Menikoff, 2019, figs 12, 13, 14 and references therein].

slope of the $D_n(\kappa)$ curve to the reaction-zone width up to the sonic point, and the sonic point moving as κ increases from the end of the slow reaction to the neighborhood of the end of the fast reaction. For PBX 9502, the steep slope for small curvature is determined by the slow reaction, while the lower slope for larger curvature is determined by the fast reaction rate in the high detonation pressure regime.

The remainder of this paper is organized as follows. In section 2 we review the assumptions of the Shaw and Johnson [1987] carbon cluster model used by the SURFplus model for the slow reaction. Section 3 describes in detail the mixture model for a partly burned HE. The form of the slow rate used by the SURFplus model is described in section 4. We conclude with a brief discussion of applying a burn model with 2 rates to either a metalized or a composite PBX.

2   Model assumptions

Assumptions based on the carbon cluster model of Shaw and Johnson [1987]:

1. The fast hotspot reaction produces small carbon clusters from excess carbon atoms in nearby reactant molecules.

2. A diffusion process leads carbon clusters to collide, stick together and the atoms to redistribute to form larger spherical cluster; *i.e.*, $C_n + C_m \to C_{n+m}$ where C_n is a spherical cluster with n carbon atoms.

3. Relative to the equilibrium, the cluster energy <u>not yet released</u> scales with the surface to volume ratio of the clusters; *i.e.*, $e_{cc} \sim N^{-1/3}$ where N is the number of atoms in the cluster.

4. For a propagating detonation wave, the cluster size increases linearly in time up to a maximum cluster size on the order of several nm which corresponds to tens of thousand carbon atoms.

Additional SURFplus assumptions:

1. The cluster distribution is characterized by the "average" cluster size (atoms/cluster)

2. Heuristically, the SURFplus model is based on a sequence of 2 reactions

$$\text{reactants} \to \text{intermediate products} \to \text{equilibrium products} .$$

with reaction progress variables

$$\lambda_1 = 1 - (\text{mass of reactants})/(\text{total mass of HE})$$
$$= (\text{total mass of products})/(\text{total mass of HE})$$
$$\lambda_2 = (\text{mass of equilibrium products})/ (\text{total mass of products})$$

where

$$\text{total mass HE} = \text{mass reactants} + \text{total mass products}$$
$$\text{total mass products} = \text{mass intermediate products} + \text{mass equilibrium products}$$

The first (hotspot) reaction uses the SURF model with reaction progress variable λ_1. For the second (carbon cluster) reaction, the SURFplus model uses the reaction progress variable λ_2 instead of the cluster size. Moreover, the carbon cluster energy is assumed to have the form

$$e_{CC}(\lambda_2) = \left(\left[\lambda_2 \, N_{\text{ratio}} + (1 - \lambda_2) \right]^{-1/3} - N_{\text{ratio}}^{-1/3} \right) Q \ , \tag{1}$$

where the energy release scales with Q, and N_{ratio} is the ratio of the final to initial cluster size; see [eq 26, Menikoff and Shaw, 2012]. We note that energy e_{cc} is a monotonic function of λ_2 with $e_{cc}(0) > 0$ and $e_{cc}(1) = 0$. Also, when $Q = 0$ the SURFplus model reduces to the SURF model.

Remark:

Other models (such as Ignition & Growth, WSD and AWSD) use 1 reaction progress variable (hence one products EOS) and account for the second reaction only in the burn rate. The first fast reaction corresponds to $0 < \lambda < \lambda_{switch}$ and the second slow reaction to $\lambda_{switch} < \lambda < 1$, where λ_{switch} is a model parameter. This can be thought of as a sequence of 2 reactions for which the first reaction completes before the second reaction starts. The PT-equilibrium EOS is used for the mixture of reactants and products over the entire domain $0 < \lambda < 1$.

3 Mixture equation of state

For the products with clusters, the SURFplus model utilizes the equilibrium products EOS with an energy offset $e_{cc}(\lambda_2)$

$$P_{prod}(V, e, \lambda_2) = P_{eq.prod}\big(V, e - e_{cc}(\lambda_2)\big) \tag{2a}$$
$$T_{prod}(V, e, \lambda_2) = T_{eq.prod}\big(V, e - e_{cc}(\lambda_2)\big) \tag{2b}$$

Thus, the EOS with clusters is based is based on the thermodynamic variables (V, e) and an explicit dependence on the reaction progress variable λ_2. It accounts for the dominant effect of carbon clusters on the products EOS with a cluster energy based on average size of the clusters. Bonding of non-carbon atoms or radicals to the surface of clusters and the associated change in products composition are implicitly included in the cluster energy.

As with the SURF model, the PT-equilibrium EOS is used for the partly burned HE (mixture of reactants EOS and products EOS, Eq. (2)), but with the energy origin shifted to account for the carbon cluster energy. The PT-equilibrium equations are

$$V = (1 - \lambda_1) \, V_{react} + \lambda_1 \, V_{prod}$$
$$e = (1 - \lambda_1) \, e_{react} + \lambda_1 \, e_{prod}$$

and

$$P(V, e, \lambda_2) = P_{react}(V_{react}, e_{react}) = P_{prod}(V_{prod}, e_{prod}, \lambda_2)$$
$$= P_{eq.prod}\big(V_{prod}, e_{prod} - e_{cc}(\lambda_2)\big)$$
$$T(V, e, \lambda_2) = T_{react}(V_{react}, e_{react}) = T_{prod}(V_{prod}, e_{prod}, \lambda_2)$$
$$= T_{eq.prod}\big(V_{prod}, e_{prod} - e_{cc}(\lambda_2)\big)$$

The standard PT-equilibrium equations (without explicit dependence on λ_2) can be recovered by replacing e with

$$\tilde{e} = (1 - \lambda_1)\, e_{react} + \lambda_1 \left[e_{prod} - e_{cc}(\lambda_2) \right]$$
$$= e - \lambda_1\, e_{cc}(\lambda_2)\ ,$$

P_{prod} with $P_{eq.prod}$ and T_{prod} with $T_{eq.prod}$; *i.e.*, the PT-equilibrium equations

$$P(V, e, \lambda_2) = P_{eq}(V, \tilde{e}) = P_{react}(V_{react}, e_{react}) = P_{eq.prod}(V_{prod}, \tilde{e}_{prod})$$
$$T(V, e, \lambda_2) = T_{eq}(V, \tilde{e}) = T_{react}(V_{react}, e_{react}) = T_{eq.prod}(V_{prod}, \tilde{e}_{prod})$$

The PT-equilibrium mixture EOS is well defined and allows the SURF rate to be calibrated using the single phase flow variables; *i.e.*, V, e, P and model parameters λ_1 and λ_2. Arguably temperature equilibrium for phase separated reactants and products (as implied by the ignition & growth hotspot concept which motivates the SURF model) is physically questionable. However, the SURF burn rate represents an average over hotspots and not the chemical reaction rate based on the average temperature. For most engineering applications, the calibration of the rate can compensate for simplifying assumptions on the mixture EOS.

Remarks:

1. The products EOS typically defines its energy origin relative to the reactants with $e_0 = 0$, in order that no energy release is explicitly needed for burning. Alternatively burning can add specific energy, $\mathsf{d}e/\mathsf{d}t = -P\,\mathsf{d}V/dt + Q\,\mathsf{d}\lambda/\mathsf{d}t$, if the products EOS has an energy offset $e_{prod} \to e_{prod} - Q$. For the SURFplus model, the energy offset is explicitly added for the energy release due to carbon clustering. Moreover, the added energy offset is a function of the second reaction progress variable and not constant.

2. The standard case of 2 reactions would have distinct EOS for the intermediate products and the equilibrium products. Energy release would result from the offsets in the energy origins of the intermediate products and equilibrium products EOS relative to the reactants. Moreover, the PT-equilibrium EOS is typically used for the mixture of intermediate and equilibrium products. This is different than the products EOS used by the SURFplus model. For the SURFplus model, one might define the intermediate products EOS as the equilibrium products EOS without the cluster energy; *i.e.*,

$$P_{im.prod}(V, e) = P_{eq.prod}\big(V, e - e_{cc}(0)\big)\ .$$

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Then the PT-equilibrium EOS would reduce to

$$P_{PT}(V, e) = P_{eq.prod}\big(V, e - (1 - \lambda_2)\, e_{cc}(0)\big) \ .$$

This is not the same as the SURFplus mixture products EOS, Eq. (2), for which

$$P_{prod} = P_{eq.prod}\big(V, e - e_{cc}(\lambda_2)\big) \ .$$

An additional energy release $\mathsf{d}(e_{cc}(0) - e_{cc}(\lambda_2))/\mathsf{d}\lambda_2 \cdot \mathsf{d}\lambda_2/\mathsf{d}t$ would need to be added to both intermediate and equilibrium energies in order for the PT-equilibrium products EOS to be the same as SURFplus products EOS.

4   SURFplus rate

The implementation of the carbon clustering reaction is qualitatively different from that of the hotspot reaction. The hotspot reaction is analogous to premixed combustion (*i.e.*, the HE molecule has both the fuel and oxidizer) and is describe by a rate law $\mathsf{d}\lambda/\mathsf{d}t = \mathcal{R}(P, T, \lambda)$. In contrast, carbon clustering involves a diffusion process analogous to laminar combustion and is not well described by a rate law with the dependent variable (P, T, λ). However, as discussed in the introduction, the dominant affect of the slow energy release from the carbon cluster reaction is on the curvature effect for propagating detonation waves. Moreover, an important property of carbon clustering from the Shaw and Johnson [1987] model is that the size of the clusters grows linearly in time.

The SURFplus model utilizes a rate that builds in the linear growth of the carbon clusters for a detonation wave and is small in the initiation regime. Let the model function for the limiting time dependence of the carbon cluster reaction progress variable be $h(t)$. An illustrative example of the time dependence of the reaction progress variable $\lambda_2 = h(t)$ and the carbon cluster energy $e_{cc}(t)$ are shown in fig. 2. The functional form for $h(t)$ [Menikoff, 2017, see Eq B.4] is linear, except for cutoffs at the start ($t = 0$) and the end of the reaction ($t_{\max}$ or $\lambda_2 = 1$ when the cluster size saturates) such that $h = \mathsf{d}h/\mathsf{d}t = 0$ at $t = 0$ and $t_{\max}$.

To smoothly extrapolate to the initiation regime when λ_1 is small and avoid an explicit time dependence, the carbon cluster rate is expressed as

$$\mathsf{d}\lambda_2/\mathsf{d}t = \mathcal{R}_2(\lambda_1, \lambda_2) = \lambda_1^2 \big(\mathsf{d}h/\mathsf{d}t\big)\big(h^{-1}(\lambda_2)\big) \tag{3}$$

where h^{-1} is the inverse function of h; *i.e.*, $h^{-1}(\lambda_2) = t$ such that $h(t) = \lambda_2$. If $\lambda_1 = 1$ throughout the second reaction then Eq. (3) would reduce to $\lambda_2 = h(t)$.

We note that the right hand side of Eq. (3) is zero when $\lambda_2 = 0$ since $\mathsf{d}h/\mathsf{d}t(0) = 0$. In order for the reaction to start, the implementation of the SURFplus model uses for the reaction progress variable $s_2 = \lambda_2^{1/2}$. Then $\mathsf{d}s_2/\mathsf{d}t = \frac{1}{2}\lambda_2^{-1/2}\mathsf{d}\lambda_2/\mathsf{d}t$ which is finite and non-zero when $\lambda_1 > 0$ since $h(t) \propto t^2$ for small t; see explicit formulae for $h(t)$ in [Menikoff, 2017, App B]. The result is that the carbon cluster reaction starts with a small rate when the hotspot reaction produces products.
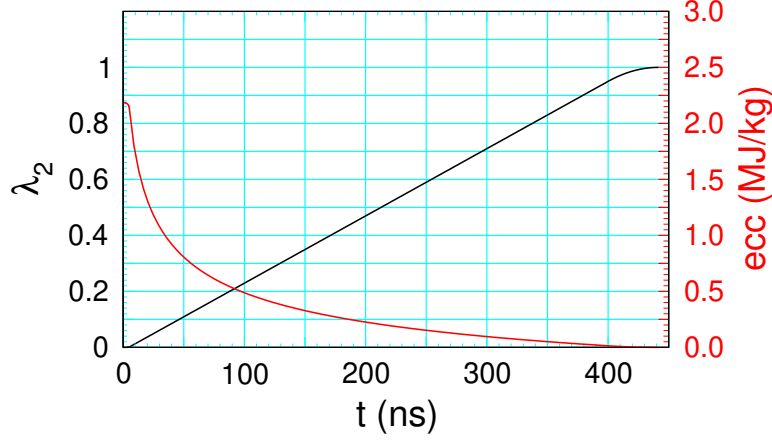
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Figure 2: Illustrative example of $\lambda_2 = h(t)$ and $e_{cc}(t)$. Curves use carbon clustering parameters for ambient PBX 9502 [Menikoff, 2017].

Remark:

> Watkins et al. [2017] have used x-Ray scattering to measure the dependence of the size of carbon clusters with distance behind the front of a detonation wave in an unconfined cylinder of PBX 9502. The diameter of the cylinder was limited to 10 mm, which resulted in a curved detonation front. To account for the front curvature and falloff in detonation pressure in the neighborhood of the HE boundary, they used a temperature cut off for a cluster to have sufficient thermal energy after collision to re-symmetrize into a sphere. The energy released by a carbon cluster depends on its surface to volume ratio. Hence its energy is greater for spherical clusters than for a network of "strands" which would form if clusters stick together but do not re-symmetrize. The cutoff (~ 2000 K for PBX 9502) would lower the cluster energy release. This could affect shock initiation before transition to detonation, corner turning (which involve much lower shock pressures and hence temperatures than the lead shock of a detonation wave) as well as the boundary layer of an unconfined rate stick. It would be straight forward to incorporate a temperature cutoff in the SURFplus carbon cluster rate.

5 Application to other PBXs

A model with 2 reactions similar to SURFplus may be useful for 2 additional classes of PBXs.

5.1 Metalized PBX

To increase the energy released by a PBX, micron sized particles of a metal such as aluminum can be added. These are called metalized explosives. The metal particles burn at a slower rate than hotspots due to the diffusion process needed to get the oxidizer to the surface of a metal particle.

Thus, the slow energy release from the metal particles can likely be modelled analogously to what the SURFplus model does for carbon clustering. The SURFplus model functions for the limiting time dependence of the metal particle size, $h(t)$, and the energy release $e_{cc}(\lambda_2)$ would need to be modified.

Due to the fast and slow reactions, a metalized explosive is expected to have the general properties that result from carbon clustering. Namely, shock ignition is dominated by the fast reaction, and the variation in the reaction-zone width would lead to a distinctive curvature effect for propagating detonation waves.

5.2   Composite PBX

Two reactions may also be useful for composite PBXs with 2 HE components; such as Comp B (TNT+RDX). When the components are phase separated, 2 parallel reactions would be applicable:

$$\text{reactants}_1 \rightarrow \text{products}_1$$
$$\text{reactants}_2 \rightarrow \text{products}_2$$
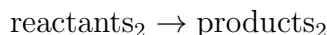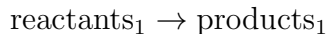
each with a reaction progress variable, a burn rate and an EOS for the component reactants and products. Pressure dependent reaction rates for the component HEs would be linked by using a PT-equilibrium EOS for the reactants and products of a partly burned PBX. The products of a fully burned composite, would rapidly become molecularly mixed and PT-equilibrium would also apply.

Alternatively, for an Eulerian hydro code such as `xRage`, this amounts to initializing HE cells with the reactants for the 2 HEs with mass fraction corresponding to that of the components of the composite, and using a PT-equilibrium EOS for mixed cells.

The two reactions would be most useful when one component is more sensitive for shock initiation and starts the reaction at low pressure, while the other releases energy faster at high pressure. For propagating detonation waves, the two component rates and energy release would likely affect the curvature effect differently than that for a single reaction model.

References

J. B. Bdzil and D. S. Stewart. The dynamics of detonation in explosive systems. *Annual Rev. Fluid Mech.*, 39:263–292, 2007. URL https://doi.org/10.1146/annurev.fluid.38.050304.092049.

R. Menikoff. SURFplus model calibration for PBX 9502. Technical Report LA-UR-17-31015, Los Alamos National Lab., 2017. URL https://doi.org/10.2172/1412839.

R. Menikoff. Accuracy of high explosive data used for reactive burn model calibration. Technical Report LA-UR-19-32062rev1, Los Alamos National Lab., 2019. URL https://doi.org/10.2172/1578002.

R. Menikoff and M. S. Shaw. Reactive burn models and Ignition & Growth concept. *EPJ Web of Conferences*, 10, 2010. doi: 10.1051/epjconf/20101000003. URL https://doi.org/10.1051/epjconf/20101000003.

R. Menikoff and M. S. Shaw. The SURF model and the curvature effect for PBX 9502. *Combustion Theory and Modelling*, 16:1140–1169, 2012. URL http://doi.org/10.1080/13647830.2012.713994.

M. S. Shaw and J. D. Johnson. Carbon clustering in detonations. *J. Appl. Phys.*, 62:2080–2085, 1987. URL https://doi.org/10.1063/1.339554.

E. B. Watkins, K. A. Velizhanin, D. M. Dattelbaum, R L. Gustavsen, T. D. Aslam, D. W. Podlesak, R. C. Huber, M. A. Firestone, B. S. Ringstrand, T. M. Willey, M. Bagge-Hansen, R. Hodgin, L. Lauder, T. van Buuren, N. Sinclair, P. A. Rigg, S. Seifert, and T. Gog. Evolution of carbon clusters in the detonation products of the triaminotrinitrobenzene (TATB)-based explosive PBX 9502. *J. Phys. Chem. C*, 121:23129–23140, 2017. URL https://doi.org/10.1021/acs.jpcc.7b05637.